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NUCLEATION AND GROWTH ✖ 10150
OF STRATOSPHERIC AEROSOLS

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INTRODUCTION

Despite early evidence of the presence of small particles in regions above the troposphere, it was only about two decades ago that the existence of a globally distributed, temporally persistent, stratospheric aerosol layer was established. Early twilight measurements by Gruner & Kleinert (1927) and Gruner (1942–1961) provided evidence that aerosols exist above the tropopause, but the first careful systematic direct measurements of change in aerosol concentration with altitude were reported by Junge et al (1961). Their *in situ* measurements showed the aerosol concentration to decrease monotonically up to and through the tropopause, a fact both expected and confirmed by other investigators (see Reiter 1971 and Junge 1963). A rather unexpected finding from these original investigations was that a globally distributed persistent stratospheric aerosol having a broad concentration maximum for large particles (radius $\geq 0.15\,\mu$m) around 20 km in elevation existed. On the basis of twilight measurements, Volz (1970) concluded that the layer persisted to the highest altitudes in the tropical latitudes, and up to an elevation of at least 25 km. However, direct measurements by Bigg et al (1970) indicated that the influence of this layer on the total aerosol content of the stratosphere persists up to approximately 37 km. Using optical radar techniques (Lidar), Schuster (1970) showed the existence of significant quasistable layers between 25 and 40 km, all presumably associated with the same sulfate layer, often termed the Junge

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layer or stratospheric sulfate aerosol layer. Numerous early investigations of the distribution of this layer were made by Junge and co-workers (Junge et al 1961, Junge & Manson 1961, Junge 1963). Its general distribution with regard to altitude and latitude was further documented by Friend (1966), Bigg et al (1970) and later by Lazrus et al (1971).

Although some investigators consider explosive volcanic eruptions to be the only source with sufficient energy to penetrate the tropopause to any great extent, early attempts (Hogg 1963, Volz 1965, Volz & Goody 1962) to correlate both the physical properties and the concentration of these aerosols with volcanic activity met with limited success. The catastrophic eruption of Mount Agung (8.5°S, 115.5°E) in March 1963 was the first well-documented major perturbation to the total stratospheric sulfate aerosol layer. Subsequent to the eruption on 18 March 1963, a marked change was noted in the nature and concentration of aerosol particles collected in the stratosphere of both the northern and southern hemispheres. Mossop (1964) reported as much as a ten-fold increase in number concentration of particles collected in the southern hemisphere following the eruption, and obtained evidence of some insoluble particles within the droplet-like phase of which the aerosol was mainly composed. Friend (1966) found a three-fold increase in particle number concentration for stratospheric samples collected during the same time periods at middle latitudes in the northern hemisphere.

Other investigators attempted to correlate volcanic activity and other perturbations such as meteoritic influx with optical measurements in both the northern (Meinel & Meinel 1963) and southern hemispheres (Hogg 1963). Volz (1965) summarized a number of optical measurements and, in addition, reported independent measurements of twilight intensity at a fixed angle of elevation prior to and following the Agung eruption (Volz & Goody 1962). Their data have the advantage of utilizing the same observational method both before and after the eruption and show that atmospheric turbidity increased by up to a factor of 20 during the latter part of 1963.

A direct quantitative comparison of data obtained by various direct and optical sampling methods is difficult to make, and the extent to which volcanoes contributed to the stratospheric aerosol layer has been the subject of some controversy. Cronin (1971) reviewed the subject and suggested that disagreement is also due to a failure among investigators to recognize the character and location of volcanic eruptions. He discussed the significance of two major belts of volcanic activity located in the arctic and equatorial latitudes, and noted that in the arctic latitudes where the tropopause is lower, eruptions may be of considerably less magnitude than those in

equatorial regions and still be of comparable importance. However, since there is a general poleward stratospheric circulation, this suggestion would have to be modified if the particles arise primarily from relatively slow gas-to-particle reactions. For a compilation of the relative magnitudes and observed trends with the dates and locations of major volcanic eruptions, the interested reader is referred to work by Cronin (1971) and Lamb (1970). Studies by Cronin (1971), and others by Hofmann & Rosen (1977) concerning the Fuego eruption, have provided important evidence concerning the origin of the stratospheric aerosol layer.

During the last decade, the group under D. J. Hofmann and J. M. Rosen and co-workers at the University of Wyoming has undertaken the most consistent studies of the change in concentration of the aerosol layer, both in altitude and in time. A summary of recent trends is given in an article by Hofmann & Rosen (1980). It is now well recognized that the early measurements of Junge and co-workers were made during a period of very low volcanic activity, and the measurements probably were made at a time when the layer was at a "background" concentration level. In an attempt to ascertain contributions to this layer, in the absence of volcanic emissions, Hofmann and Rosen have compared their concentration measurements in recent years with those of Junge in the 1959 to 1960 time period. Based on this comparison, there seems to be as much as a 9% per year increase in aerosol concentration, which Hofmann & Rosen suggested may be due to anthropogenic activities. Even though a careful comparison of concentrations measured by various techniques was made, this conclusion is, of course, speculative at this point. In addition, the comparison by Hofmann & Rosen suggested an increase in the upper troposphere over the same period. No generally accepted mechanisms of origin have been proposed that account for this increase.

Early study of the stratospheric aerosol layer was prompted by curiosity concerning the upper atmosphere surrounding the earth. However, more recently there has developed considerable concern about the impact of this aerosol layer on the earth's environment, especially its contribution to the earth's total albedo. Because of both size range and location, stratospheric aerosols tend to scatter the earth's incident radiation and are believed to have had an impact on the earth's global temperature following certain major volcanic eruptions (Lamb 1970). In this context the aerosol layer can have a direct impact on climate, and since climate has a direct bearing on agriculture as well as on the energy needs of the nation and the world, there has been a considerable growth of interest in the nature, formation, and distribution of the stratospheric aerosol layer. The climatic effects due to volcanic eruptions are reviewed by Toon & Pollack (1980).

In addition to their role in scattering sunlight, atmospheric aerosols might affect climate if they have a substantial impact on certain atmospheric chemical reactions. Particles themselves potentially provide a reservoir whereby gas-phase constituents can be removed from participating in further homogeneous reaction mechanisms. Furthermore, although no definitive evidence currently exists, calculations have suggested that aerosols may play a role as heterogeneous catalytic sites in certain reactions (see section on the role of aerosols in the upper atmosphere). Finally, since ions readily charge exchange with aerosols upon collision, the presence of aerosols has a potential bearing on ion concentration in the upper atmosphere. Aerosols may, therefore, partly govern atmospheric electrical parameters.

FORMATION MECHANISMS

The pioneering studies of Junge established that a substantial component of the stratospheric aerosol layer is sulfate. As a result of the work of Lazrus and co-workers (Cadle et al 1970, Lazrus & Gandrud 1974), these aerosols also are known to contain elements such as Si, Na, Cl, Mn, Br, and Ca.

Early speculations that the aerosol layer might be formed as a result of tropospheric aerosols carried upward into the stratosphere or as the result of meteoritic ablation products are inconsistent with some of the compositional findings. This, and the surprising finding that sulfate represented the most abundant single chemical component of the aerosol, led to extensive work to ascertain the origin and mechanisms of sulfate aerosol formation (see Friend 1966, Shedlovsky & Paisley 1966). Although early measurements indicated that the sulfate ions were chemically combined with ammonium ions, studies by Manson et al (1961) indicated that this conclusion must be viewed with caution. Handling procedures often introduce ammonia as contamination, which sometimes leads to the formation of ammonium sulfate by subsequent reactions *after* collection.

More recent compositional analysis of the stratospheric aerosol by Lazrus & Gandrud (1974) suggests that the quantity of cations (other than protons) is insufficient to chemically balance the sulfate. Consequently, it is generally assumed that sulfuric acid represents the major component of stratospheric aerosol.

Toon & Pollack (1973) concluded that, from a thermodynamic point of view, sulfuric acid droplets should be stable at the temperature and water vapor concentrations of the stratosphere. This conclusion follows from the fact that the partial pressures of both sulfuric acid vapor and water vapor

in equilibrium with concentrated sulfuric acid solutions are very low at stratospheric temperatures. The authors estimate that the stratospheric droplets should be either a supercooled liquid or a solid composed of an approximately 75% sulfuric acid solution. Attempts to ascertain chemical composition have been made by Rosen (1971) in which the stratospheric aerosol was evaporated *in situ*, and its temperature of evaporation measured. These findings also indicate that a 75% sulfuric acid solution is the major portion of the aerosol.

In early publications, Junge and his co-workers provided circumstantial evidence that the sulfate aerosols were not being carried directly into the stratosphere but were most likely generated by gas-to-particle conversion reactions of SO_2 or H_2S imported into the stratosphere (Junge et at 1961). Subsequently, Castleman et al (1974) made a detailed study of the sulfur isotopic ratio of the stratospheric aerosol, which led to similar conclusions. The observations of Castleman et al have shown that during periods of large volcanic eruptions sulfate aerosol is generated by an *in situ* oxidation mechanism rather than by simple input of tephra from the original eruption cloud. Studies of the oxidation of SO_2 with OH (Castleman & Tang 1976/77, Moortgat & Junge 1977) have indicated that these reactions may be dominant in the formation of the stratospheric aerosol layer from SO_2 generated by input via the volcanic eruptions.

It is well known that various sources of sulfur compounds have specific ratios of ^{32}S to ^{34}S and that this isotope ratio can be used as an indication of the original source of the sulfur, if some measure of potential reactions is taken into consideration. A systematically varying trend in the isotopic ratio following input of the reactive species may provide further information on subsequent chemical reactions. A clear correlation between sulfur concentration and volcanic activity was found from the data of Castleman et al (1974). The perturbation to the total stratospheric dust burden by the paroxysmal eruption of Mount Agung has been well documented and there was a large change in the sulfate concentration as well. The data show that the sulfate concentration in the southern hemisphere increased by approximately two orders of magnitude within a year after the eruption but took some seven months or more to reach a peak concentration. Tephra are known to settle out relatively rapidly, and it must be concluded that this increase in sulfate concentration is evidence for a gas-to-particle conversion mechanism.

Further evidence for a gas-to-particle conversion mechanism was established by considering the isotopic ratios of sulfur for a similar time period. Characteristic trends are invariably observed following a major volcanic event. The data show an abrupt decline in the ^{34}S enrichment following

the eruption of Mount Agung and a much smaller decline in magnitude after the smaller eruption of Fernandina. The trends with time and altitude provide very good evidence for an *in situ* formation process (Castleman et al 1974). After the passage of several years without another major eruption, the isotopic ratios always show a tendency to return to preeruption values.

The data have been interpreted by recognizing that for short time intervals following major eruptions the additional sulfate contribution by all other processes is comparatively negligible, and the observed continual change in the sulfur isotopic composition for stratospheric aerosols is the result of fractionation processes. Since fractionation would not be expected on a purely physical basis after a few days following an eruption, these changes are clearly indicative of an *in situ* reaction. As a reaction proceeds to completion, the sulfate product would be expected to exhibit a unidirectional change in isotopic composition over a time span related to the eruption.

Isotopic data for sulfur also suggest a common source of sulfur in the stratosphere in both the northern and southern hemispheres, indicating that in the absence of major volcanic eruptions the sulfate in the two hemispheres probably has a common origin. It is speculated that biogenic sulfur released into tropical upwellings may be this source. Most of the tropospheric sulfur compounds such as SO_2, H_2S, and dimethyl sulfide are believed to be sufficiently reactive as to make it unlikely that these compounds would survive in the troposphere long enough to diffuse in sufficient quantities into the stratosphere (Crutzen 1976). Based on these considerations, Crutzen has suggested that stratospheric aerosol formation in the absence of direct sulfur injection by volcanic eruptions may result from the diffusion of OCS into the stratosphere where it becomes photodissociated, eventually reacts to SO_2 and subsequently converts to sulfate aerosol. CS_2 might also make a minor contribution to the stratospheric aerosol layer. Recent measurements of stratospheric sulfur compounds (Inn & Vedder 1980) seem to bear out this conclusion.

NUCLEATION

An aerosol is formed when a gas-phase species undergoes a phase transformation to condensed-phase particles. This process may proceed via a nucleation mechanism involving (a) stepwise clustering of gas-phase molecules or (b) interaction between small molecular clusters of the aerosol-forming species. The development of an aerosol and its size distribution can in principle be completely described by a general dynamic equation (Gelbard & Seinfeld 1979), which describes the formation and loss pro-

cesses for the spectrum of particles ranging from gas molecules through small molecular clusters to large aerosol particles. However, the complete kinetics required to solve this equation are not generally known, especially in the case of the formation and interaction of molecular clusters containing only tens of molecules. Therefore, the formation of an aerosol particle is often treated as a problem separate from the other processes such as condensation and coagulation. Following this pattern, the present section of the review first considers aerosol formation and then aerosol growth processes as applicable to the stratosphere. Many of these general processes for aerosols are treated in several recent texts (Pruppacher & Klett 1978, Friedlander 1977, Twomey 1977).

Nucleation processes may be classified according to the material basically responsible for inducing nucleation. These are (a) homogeneous, (b) heterogeneous, and (c) heteromolecular. In the homogeneous case only those molecular species that constitute the condensing phase are involved in the nucleation process. Heterogeneous nucleation operates when these species condense onto the surface of a foreign body. In the heteromolecular case, a molecular entity acts as the foreign body that induces the nucleation of the condensable components.

A further distinction among the nucleation processes is made to denote the number of condensable substances that participate simultaneously to form new aerosol particles. Thus, nucleation may be unary, binary, ternary, etc. It should be noted that in the literature binary homogeneous nucleation is often referred to as heteromolecular nucleation, and so confusion with the above definition should be avoided.

Classical nucleation theory (see Pruppacher & Klett 1978) assumes that a quasi-steady state population of molecular clusters exists and that the rate of nucleation or aerosol formation is determined by the rate of collision of the monomeric gas molecules with critical clusters. The critical cluster is that cluster which corresponds to a free energy maximum during its growth starting from a free gas-phase molecule to a condensed-phase particle. The nucleation barrier $\Delta G^{\ddagger}$ is then the difference between this free energy maximum and the free energy minimum corresponding to the most stable subcritical (i.e. smaller) cluster. Thus, the nucleation rate J is expressed in terms of a Boltzmann-type relation, which determines the critical cluster concentration, given by

$$J = K_{exp}(-\Delta G^{\ddagger}/kT), \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature, and the preexponential factor includes terms that express the collision dynamics of the monomer with the critical cluster and the deviation of the quasi-steady state population of critical clusters from a constrained equilibrium

one. This formulation neglects any contribution of forming aggregates larger than the critical size by means of cluster-cluster collision. However, during heterogeneous or heteromolecular nucleation, a stable small cluster population may exist and cluster-cluster interactions should not be ignored. Zurek & Schieve (1980) have shown that even for homogeneous nucleation cluster-cluster interactions can be important under some circumstances.

The demarcation between whether an aggregate of molecules is a gas-phase cluster or a condensed-phase aerosol particle, i.e. the point at which nucleation has occurred and growth commences, is not intuitively well defined. From nucleation theory this point can be thermodynamically defined by the critical cluster size, since further growth by condensation for particles larger than this size is assured. When no nucleation barrier exists, a critical cluster is not defined thermodynamically and nucleation is limited only by the kinetics of the forward growth rates. In this case, no dividing line exists. In practice, the critically sized cluster is not directly observed, and the properties of nucleation are inferred from the aerosol particles that are observed. Therefore, the demarcation may be conveniently defined by a minimum detectable particle size.

When a nucleation barrier exists, the problem of determining the nucleation rate is largely one of calculating the requisite free energy changes. Furthermore, this calculation is necessary to determine under what conditions the barrier disappears. The most broadly applicable approach is the use of the capillarity approximation, often called the Thomson drop model, which is based on the properties of the bulk phase. In this model the free energy of forming a cluster of n molecules from the monomeric gas is due to condensation of n molecules, the formation of a surface, and effects due to a foreign nucleus if any. For the unary homogeneous case, a spherical drop of n molecules, the free energy is expressed by the equation

$$\Delta G(n) = -nkT \ln S + 4\pi r^2 \sigma, \tag{2}$$

where r is the radius (related to n by the density of the condensed medium) of the drop, and σ the surface tension. The saturation ratio S is defined as the partial pressure p of a component divided by its vapor pressure p_0 over the bulk condensed phase. Whenever a system is supersaturated ($S > 1$), the first term of Equation (2) is negative and favors cluster growth. The second term is responsible for the existence of the nucleation barrier and is commonly referred to as the Kelvin effect. In other words, the surface energy results in a higher vapor pressure for a curved drop than for a flat surface of bulk. The Kelvin effect is such that the vapor pressure of a water drop of 0.1 μm radius is about 2% higher than that for a flat surface and

about 25% higher for a 0.01 μm radius drop. Evidence in support of this effect and its validity is reviewed by Skinner & Sambles (1972).

A macroscopic interpretation of a surface with a surface tension in nucleation theory, however, is at best questionable when one considers critical clusters of typically a few tens of molecules. However, the Thomson model remains popular because of its simplicity and its relative success in interpreting experimental results (Jaeger et al 1969, Castleman et al 1978). Another approach using macroscopic-type parameters is the Fisher droplet model (Stauffer & Kiang 1977).

Molecular models using statistical mechanics (Hale & Plummer 1973, Hoare et al 1980) to calculate cluster properties have a firmer theoretical footing and qualitatively produce results similar to macroscopic models. However, such models are not as yet applicable to problems of stratospheric nucleation because of their complexity and the lack of the necessary information. Recent computer simulation techniques such as Monte Carlo (Abraham 1974) and molecular dynamics (Briant & Burton 1975) methods circumvent the necessity of directly determining thermodynamic quantities. Using these methods, Zurek & Schieve (1978) have confirmed the concept of a critical cluster. As with molecular models, these methods have been limited to the treatment of only very elementary systems.

NUCLEATION IN THE STRATOSPHERE

Assuming water and sulfuric acid as the primary components, the requirement that a gaseous constituent must be supersaturated with respect to a condensed phase in order to initiate the formation of an aerosol eliminates unary homogeneous nucleation as a viable mechanism for the creation of a stratospheric aerosol. The vapor pressure at stratospheric temperatures (around $-50°C$) of water and sulfuric acid over their pure solutions are well above the measured partial pressures of water and estimated sulfuric acid vapor concentrations (Hamill et al 1977a). More recently, the existence of low sulfuric acid concentrations in the stratosphere has been supported experimentally by Arnold & Fabian (1980). Similarly, the unary heterogeneous or heteromolecular process could only occur if the vapor pressure is reduced by the foreign nucleus as, for instance, a "soluble" particle. However, a particle that may be soluble in the bulk phase may not act as a soluble nucleus as far as nucleation is concerned. A critical saturation must be exceeded in order that the soluble crystal absorb a sufficient number of solvent molecules to dissolve. With water, for instance, the critical saturations are 0.55 (55% relative humidity) for sodium sulfate and 0.76 for sodium chloride (O'Brien 1948). The relative humidity of the

stratosphere is typically below 1% so that such salts will behave as insoluble nuclei. Since water is much more abundant than sulfuric acid and the acid itself is hygroscopic, self-nucleation of sulfuric acid onto an acid soluble crystal is improbable. Consequently, any discussion of nucleation in the natural stratosphere must include at least a binary process.

Binary Nucleation

As discussed in the foregoing section, binary nucleation is the most likely mechanism to lead to new particle formation in the stratosphere. When two pure substances are mixed, the vapor pressures of the individual components over that mixture may be lower than those over their pure states. Thus, a supersaturation in a mixed system may develop without the supersaturation of any single component with respect to its pure state.

In the Thomson formulation for the homogeneous case, the free energy of forming a drop of a composition defined by the number of molecules n_i of each component is given by the equation

$$\Delta G(n_1, n_2, \ldots n_l) = -kT \sum_{i=1}^{l} n_i \ln \frac{p_i}{p_{0i}} + 4\pi r^2 \sigma, \tag{3}$$

where p_i is the partial pressure of the ith component, and p_{0i} is its vapor pressure over a bulk solution of the composition determined by $(n_1, \ldots, n_l)$. The determination of the free energy barrier to nucleation in the critical size and composition is complicated by the fact that σ, p_{0i}, and the solution density to which r is related are implicit functions of the variables $n_1, \ldots, n_l$. Yue (1979) concisely described the various numerical and graphical methods that have been applied to determine these properties for a binary system (where l equals 2).

In the stratosphere the gaseous concentration of sulfuric acid molecules is much less than that of water. Therefore, a cluster or aerosol particle is quickly equilibrated with respect to water vapor, and the clustering and growth is determined by the collision rate of sulfuric acid molecules with these clusters and aerosol particles (Mirabel & Katz 1974). Consequently, the ratio p_i/p_{0i} for water may always be assumed to be unity.

Ternary Nucleation

The preceding discussion has considered only the simultaneous nucleation of two components since sulfuric acid and water are thought to be the major condensable species in the stratosphere. However, the possibility that three components promote nucleation under stratospheric conditions had been suggested by Kiang & Hamill (1974), with nitric acid as the third component. Kiang et al (1975a,b) subsequently extended nucleation theo-

ry to ternary systems and considered the nitric acid sulfuric acid water system in the stratosphere. Unfortunately, vapor pressure data of ternary systems, particularly at stratospheric temperatures, are largely lacking. The suggestion by Kiang & Hamill (1974) that nitric acid might be saturated in the stratosphere with respect to HNO_3-H_2SO_4-H_2O solutions containing a significant amount of nitric acid (about 15% by weight) was based on an admittedly crude extrapolation using data available in the International Critical Tables (Zeisberg 1928) which are from several different sources and are evidently inconsistent when examined carefully. The low vapor pressures deduced by Kiang & Hamill's extrapolation for 15% nitric acid solution appear to arise from this inconsistency.

At present no evidence exists for nitric acid participation in stratospheric aerosol formation (Lazrus & Gandrud 1974). One should note, however, that compositional analysis of aerosols may also be misleading in distinguishing between the possible nucleation processes. The composition of stratospheric aerosols has routinely been determined at room temperature where a component may become relatively more volatile than at stratospheric temperatures. On the other hand, a ternary mixture may develop subsequent to nucleation due to the reaction of aerosol particles with other gaseous species. The possibility of ternary nucleation cannot as yet be discounted until more adequate data such as partial pressures of gaseous species over mixed systems becomes more readily available.

Binary Heterogeneous Nucleation

Hamill et al (1977a) have shown that homogeneous processes are very improbable due to the general availability in the stratosphere of foreign nuclei along with preexisting aerosol particles. The nuclei include particles transported into the stratosphere from tropospheric, extraterrestrial, or volcanic sources (Castleman 1974). Nuclei created *in situ* are generally of molecular dimensions such as ions and, therefore, may create aerosol particles via heteromolecular nucleation, which is discussed in the next subsection.

Usually nuclei of tropospheric, volcanic, or extraterrestrial origin are large in comparison to the critical size of homogeneous nucleation. These nuclei would actually be aerosol particles in their own right. Heterogeneous nucleation as applied to the stratosphere may be considered a conversion of a non-sulfate aerosol into a sulfate-containing aerosol. The heterogeneous process on insoluble nuclei, which act only as sites for the sticking of the nucleating phase, modifies the surface energy required to reach the critical size. For instance, for a completely "wettable" nucleus of radius r_0 the surface free energy of forming a drop of radius r is given by $4\pi(r^2 - r_0^2)\sigma$ since the bare nucleus plus the monomeric gas molecules is

the reference state of the system. If r_0 is larger than the critical radius, then no nucleation barrier would exist, and nucleation would be kinetically controlled by the time required to "wet" the nucleus.

For the case of a partially wettable nucleus, the macroscopic concept of a contact angle φ is often employed (see Chapter 12 in Pruppacher & Klett 1978). For a completely wettable nucleus, the contact angle is $0°$, whereas for a completely non-nucleating unwettable nucleus φ would be $180°$. Basically, the contact angle determines the curvature and consequently the surface energy of the nucleating medium on a nucleus of a given shape or radius. A soluble nucleus would affect the vapor pressure in the system and act as a completely wettable nucleus.

Nucleation on completely wettable insoluble nuclei has been calculated to be a very effective mechanism (Hamill et al 1977a). However, the problem of the "wettability" of these nuclei has not been adequately addressed, and Farlow et al (1977) found that undissolved granules are present in only about one third of the stratospheric aerosol particles during periods of low volcanic activity. In addition, the number of such nuclei in the stratosphere is still uncertain. Measurements with condensation nuclei counters (Podzimek et al 1977) cannot uniquely distinguish between particles formed in the stratosphere and those transported to it from other sources.

Heteromolecular Nucleation

IONS   Due to the electrostatic forces whereby neutral molecules, especially polar ones, readily cluster around an ion (see Castleman 1979) ion-induced nucleation is known to happen preferentially to homogeneous nucleation. The continual ionization of the stratosphere (see Meyerott et al 1980) provides a significant source of ions. If the lifetime against neutralization for the clustering ion is sufficiently long compared to the time required to induce nucleation, then this mechanism may be operative. The average lifetime of an ion in the stratosphere is around 10^3 seconds, but the low sulfuric acid concentration implies slow H_2SO_4 clustering rates onto ions. Therefore, clustering kinetics, instead of thermodynamics as assumed in classical nucleation theory, limit ion-induced nucleation in the stratosphere.

Nevertheless, Castleman & Tang (1972) established that small ion clusters actually represent a segment of the overall size distribution of atmospheric species. Chan & Mohnen (1980) estimated a stable ion cluster distribution and relative critical cluster population using the Thomson drop model for the binary sulfuric acid–water system. The Thomson model is a very crude assumption in that specific ion-neutral interactions are not accounted for. Evidence now exists that stratospheric negative ions are mixed clusters of acids such as nitric acid, sulfuric acid, and possibly hydrochloric acid, while positive cluster ions contain water and possibly

sodium hydroxide or sodium chloride (see Viggiano et al 1980, Ferguson 1978). The rather specific acid-base type interactions of ions of opposite charge invalidate the use of the simple Thomson theory to predict the type of cluster ions present in the stratosphere.

Since ions form small stable clusters at a concentration of a few thousand per cubic centimeter, an attractive hypothesis is that ion cluster-cluster interactions may be important in producing nuclei upon which condensation can eventually occur. Mohnen (1971) first suggested this possibility. Since clustering stabilizes an ion by effectively reducing the ionization potential of positive ions and increasing the electron affinity of negative ones, E. E. Ferguson (1977, private communication) subsequently pointed out that although the neutralization of oppositely charged ions may be exothermic, clustering may cause the charge neutralization of two ions to be endothermic so that their combination could produce a stable solvated ion pair. One should note that the products of ion-ion collisions and the stability of many of the feasible ion-neutral association clusters in the stratosphere are not known. Consequently, the degree of clustering required for a pair of ions to form a solvated ion pair in contrast to dissociated neutral products can at present only be qualitatively estimated.

Since an ion pair has a large dipole moment, Arnold (1980) has suggested that further clustering of these ion pairs with ions to create multi-ion complexes may effectively promote nucleation by producing small electrolytic droplets as nuclei upon which condensation can occur. In this case, of course, classical nucleation theory is quite inadequate for describing the rate of phase transformation and, therefore, aerosol formation.

RADICALS   The reaction $OH + SO_2 + M \rightarrow HSO_3 + M$ is recognized as an important loss mechanism of sulfur dioxide (Castleman & Tang 1976/77). The formation of aerosols initiated by this reaction in the presence of water from which OH is formed by photolysis is also well established (Davis et al 1979). Niki et al (1980) have spectroscopically shown that the products appear to be liquid sulfuric acid containing varying amounts of water. However, the role of the HSO_3 radical in forming the aerosol is not understood. Friend et al (1973) have demonstrated that the products of the photolysis of H_2O-SO_2-O_2 mixtures rapidly produce aerosol particles when introduced into a condensation nuclei counter in which the count rate (related to the nucleation rate) is dependent on the initial relative humidity of the preceding reaction zone. Friend et al (1980) have suggested that single sulfur molecules such as $H_2S_2O_6$, $H_2S_2O_8$, SO_3, or H_2SO_4 act as nuclei analogous to ions in ion-induced nucleation in the highly supersaturated condensation counter. These sulfur compounds are possible products in reactions or combinations of the free radicals created in the reaction zone. Another possibility is that the production rate of sulfuric

acid is sensitive to humidity due to the reaction chemistry of hydrated radicals such as HSO_5, $HSO_5 \cdot H_2O$, and $HSO_5 \cdot 2H_2O$.

Davis et al (1979) have estimated that the dominant initial reaction path for HSO_3 in the stratosphere should be association with O_2. Association of water molecules to these radicals may also occur. The number of associated water molecules will be dependent on the relative humidity analogous to the cases for H_2SO_4 (Heist & Reiss 1974) or ions (Castleman & Tang 1972). In general the prevalence and role of neutral association complexes in atmospheric phenomena has been considered only recently (Carlon 1979, Calo & Narcisi 1980) and deserves quantitative investigation.

In regard to the stratosphere Davis et al (1979) have established that reactions of sulfur radicals with radicals such as NO_2 may also be competitive pathways. Interestingly, species such as $NOHSO_4$ (Farlow et al 1978) and $(NH_4)_2S_2O_8$ (Friend 1966) have been tentatively identified in samples of stratospheric aerosols. Such compounds as $H_2S_2O_6$, $H_2S_2O_8$, and $NOHSO_4$ are also known to decompose or hydrolyze to sulfuric acid in acidic solutions, for example (*Gmelins Handbuch* 1960),

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5, \qquad (4)$$

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2. \qquad (5)$$
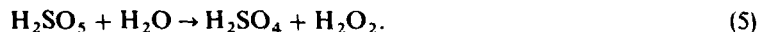
GROWTH

Aerosol particles may grow by coagulation, scavenging, condensation, or gas-aerosol reactions; the reverse process, namely, evaporation, must also be considered.

In the stratosphere the coagulative process due to Brownian diffusion is of primary importance. Gravitational coagulation, which results from a larger particle falling at a net rate with respect to a smaller one, is unimportant in the stratosphere (Turco et al 1979). Also, coagulation due to turbulent motion is usually not relevant to stratospheric conditions.

The general treatment of Brownian coagulation for stratospheric aerosol is complicated by particle dynamics. The particle size ranges of interest occur in a transition region where neither free molecular kinetic nor slip flow diffusive kinetic motion are fully applicable (Castleman 1974). Equations have been formulated to interpolate this region so as to approximate the particle dynamics over the entire range from free molecular to diffusive motion (Fuchs & Sutugin 1971).

Whether condensation or evaporation operates on an aerosol particle depends on the sulfuric acid vapor pressure at given conditions. An aerosol particle is generally assumed always to be essentially in equilibrium

with the surrounding water vapor. Thus, at a given temperature water vapor concentration determines the concentration of sulfuric acid in the aqueous sulfuric acid aerosol particle. This in turn specifies the sulfuric acid vapor pressure over the particle (Toon & Pollack 1973). Evaporation of the particle occurs if the sulfuric acid partial pressure is less than its corresponding vapor pressure. Condensation occurs in the opposite case. During these processes the water content of the aerosol is adjusted practically instantaneously on the time scale of sulfuric acid addition or loss to maintain its equilibrium. Whereas coagulation decreases the total number of aerosol particles and shifts the size spectrum to larger particles, condensation has no direct effect on the total particle concentration. Many of the details of coagulation and condensation are discussed by Hamill et al (1977b).

The scavenging of molecular clusters by aerosol particles lies between the domain of coagulation and condensation. All three processes are necessary to describe the effect of an existing aerosol on the total size spectrum. The major significance of scavenging is its effect on the steady-state molecular cluster distributions and consequently on heteromolecular and homogeneous nucleation (Gelbard & Seinfeld 1979). The decrease of nucleation rates by a preexisting aerosol represents a feedback mechanism such that a balance is created between the total aerosol surface area and the particle production rate required to maintain that aerosol against losses due to sedimentation of large particles (see McMurry & Friedlander 1979). For the stratosphere, however, the contribution to the aerosol of particles transported from volcanic, tropospheric, and meteoric sources needs to be considered to establish the magnitude of *in situ* particle production. At present only rough estimates of these contributions exist (Turco et al 1979, Hunten et al 1980).

The reaction of gases with an aerosol, i.e. heterogeneous chemistry, may also lead to growth of the particle. For example, sulfur species may be absorbed and directly oxidized to sulfuric acid within the aerosol particle, or gaseous species may react with the sulfuric acid in an aerosol particle to form salt species. The kinetics of such reactions may be controlled by either surface or volume characteristics (see Friedlander 1977). At present the details of gas-aerosol heterogeneous chemistry are poorly understood and only a limited amount of quantitative data exists (Baldwin & Golden 1979).

NUCLEATION AND GROWTH IN MODELS

Since the discovery of the sulfate aerosol layer, its formation and properties have been the object of several modeling efforts. In an attempt to explain observed condensation nuclei distributions, Junge et al (1961)

developed a model in which sedimentation, diffusion, and coagulation were considered. The particle source was implied by fixing particle number densities at the top and bottom altitudes of the model, and aerosol formation as well as condensation and evaporation of aerosol particles was neglected. Despite this, the model helped to explain some observations of condensation nuclei distribution. Burgmeier & Blifford (1975) also considered basically only sedimentation, diffusion, and coagulation but included an empirical source term to balance the loss of aerosols by sedimentation.

In a subsequent modeling attempt, Rosen et al (1978) introduced a fixed H_2SO_4 distribution where the mixing ratio was defined by a narrow Gaussian distribution centered at 20 km altitude. This model allowed condensation, but evaporation was ignored as no significant fraction of aerosol particles in the model reached the model's upper boundary level. The important advancement in this model was that the supply of sulfuric acid was explicitly considered.

Most recently, Turco et al (1979) included evaporation and nucleation. In addition, the H_2SO_4 concentration was calculated interactively within the aerosol model. Thus, the concentration of sulfuric acid depended on the rate of production of sulfuric acid (based on a simple chemical scheme to oxidize sulfur species) versus that of its incorporation into the aerosol particles. Nucleation was assumed to proceed by heterogeneous nucleation onto chemically inert nuclei transported from the troposphere. The nucleation rate was taken to involve a fixed induction time (10^6 seconds) required before condensation could occur on these nuclei. Toon et al (1979) demonstrated that an order of magnitude variation in time did not significantly affect the model results. These models have successfully explained many of the observed properties of the stratospheric sulfate aerosol. Although several details are simplified or ignored, they have significantly contributed to understanding the relative importance of various mechanisms in determining the features of the stratospheric aerosol.

ROLE OF AEROSOLS IN THE UPPER ATMOSPHERE

Potentially important chemical and physical effects may be divided into three categories. These include charge exchange between ions and aerosols, surface catalysis, and the production of trace species. In this regard, the aerosol may provide a sink or source for some gas-phase constituents. Rough estimates of the surface area in the stratospheric aerosol layer based on particle size distributions indicate about 10^{-8} cm^2 cm^{-3}. Based

on these values and an elementary kinetic theory analysis, a given gas-phase molecule suffers a collision with a stratospheric aerosol surface approximately every 10^4 to 10^5 seconds.

There is one situation where stratospheric aerosols have been thought to play a role in the production of trace species, namely, the production of HCl from the interaction of H_2SO_4 with NaCl (Castleman et al 1975). Calculations show that the reaction is exothermic and the quantity of HCl so produced is likely to be limited by the quantity of NaCl, potentially from sea salt, which may be deposited in the stratosphere following major storms in equatorial regions. However, the kinetics of the reactions are not known under the low temperature conditions prevailing in the stratosphere, and laboratory studies of this reaction are needed.

There are three possible ways in which aerosol surfaces may play a role in affecting the gas-phase concentration of chemically reactive species. These include 1. the destruction of reactive intermediates such as free radicals, which would be normally important in gas-phase reactions, 2. a catalytic influence on reactions between stable gas-phase constituents, or 3. the stabilization of a product molecule in the condensed state, which might otherwise readily dissociate in the gas phase.

Quantitatively, very little is known about catalytic reaction mechanisms or rates that might be important in the upper atmosphere. Therefore, in order to assess which mechanisms warrant attention, model calculations were made where it was assumed that one species is adsorbed and others react with it upon each collision (Castleman et al 1975). By comparing these rates to known homogeneous ones involving the same species, a crude prediction was made regarding what species might have potentially important surface-controlled chemistry. Admittedly this does not provide an unequivocal assessment of the importance, or lack thereof, for the species under consideration, but it gives a way of screening and establishing priorities for laboratory investigation. Table 1 is a list of reactants, possible products, and an estimate of the maximum possible ratio of heterogeneous to homogeneous rates.

Much of the stratospheric aerosol is believed to be composed of H_2SO_4, which is notoriously non-catalytic for most reactions. Based on the listing in Table 1, few of the systems warrant any attention whatsoever, especially if H_2SO_4 is assumed to be distributed over all surfaces to an equal extent (a condition that is suspected but not as yet established with any certainty). Yet, since sulfuric acid aerosols contain H_2O, reaction with N_2O_5 might be important and deserves attention in this context. Olszyna et al (1979) have shown that ozone destruction is not important on sulfuric acid surfaces. Therefore, this marginally important case may be omitted from further consideration unless substantial metallic oxide aerosols are found,

Table 1 Comparison of surface and gas-phase reaction rates[a]

Reactants	Products	Ratio, surface to gas-phase reaction rate
N_2O_5, H_2O	$2 HNO_3$	$> 10^3$
NO_2, O_3	NO_3, O_2	~ 10
CH_3O_2, NO	CH_3O, NO_2	~ 1
O_3, O	$2 O_2$	200
NO, O_3	NO_2, O_2	~ 10
$HO_2\cdot$, O_3	$OH\cdot$, O_2	5.3×10^{-2}
$OH\cdot$, O_3	$HO_2\cdot$, O_2	1×10^{-3}
$CH_3O\cdot$, O_2	$CH_2O\cdot$, $HO_2\cdot$	1.6×10^{-5}
$Cl\cdot$, O_3	$ClO\cdot$, O_2	1×10^{-6}
$O\cdot$, O_2	O_3	2.5×10^{-7}
$CH_3\cdot$, O_2	$CH_3O_2\cdot$	5.8×10^{-8}
$H\cdot$, O_2	$HO_2\cdot$	1.7×10^{-10}

[a] Maximum surface reaction rate based on kinetic theory for collision rates, and assuming unit reaction probability upon collision.

in which case they may play a somewhat important role. [Ferguson (1978) suggests the possible importance of ozone reactions with metal atoms which might be a source of oxide aerosols.]

Three other possibly important surface reactions are the reaction of ClO with H_2SO_4/H_2O to produce HCl (Martin et al 1978). $ClONO_2$ with H_2O giving rise to HOCl (J. W. Birks 1979, private communication), and sulfur dioxide by H_2O_2. There is some evidence, based on laboratory measurements, that the first reaction occurs to a small extent. Estimates suggest that the inclusion of this reaction in models could decrease by a few percent the estimated Cl/HCl ratios existing in the stratosphere (Martin et al 1978). Laboratory studies are needed to assess the importance of surface reactions with $ClONO_2$. There are no laboratory data suitable for assessing the potential importance of SO_2 reaction with H_2O_2 on surfaces (Cadle et al 1975).

A consideration of the potential importance of stratospheric heterogeneous reactions on the behavior of the fluorocarbons has failed to provide any evidence in support of such a mechanism. Ausloos et al (1977) have demonstrated that unexpectedly large surface photochemical effects can result on certain surfaces, notably certain sands, leading to the destruction of some fluorocarbon compounds and N_2O. The mechanisms and significance of these catalytic processes are not well known,

but even if they do occur, the quantity of potentially active surface material is far too low to be of importance in the stratosphere.

Ion concentrations are established by the balance between the rates of formation and destruction. The latter is the result of two processes and includes recombination between negative and positive ions, and the process of ion charge exchange with free surfaces provided by aerosol particles. Studies (Keefe et al 1959) show that to a good approximation aerosols maintain a Boltzmann charge distribution. The rate of change of ion concentration n is given by

$$\frac{dn}{dt} = Q - \alpha n^2 - n\left(\beta A\right), \tag{6}$$

where t is time, Q ion production rate, α recombination coefficient for negative and positive ions, β the coefficient of ion attachment to aerosols, and A the aerosol surface area.

The stratosphere contains approximately 10^3 ion pairs/cm^3. Under stratospheric conditions, the recombination coefficient α is 10^{-7} to 10^{-6} cm^3/sec from which it follows that the ratio of the loss of ions due to mutual recombination to that due to charge exchange upon collision with an aerosol particle is

$$\frac{\alpha n}{\beta A} \approx 10. \tag{7}$$

Therefore, the charge exchange process with aerosols are of only secondary importance except when the aerosol concentration is increased following periods of intense volcanic activity.

CONCLUSION

Various sampling studies and numerical models have provided evidence that the in situ oxidation of sulfur-bearing gases (Junge & Manson 1961, Turco et al 1978) is responsible for the sulfate mass of the stratospheric aerosol. An extensive study of the temporal and spatial distribution of the sulfur isotope ratio by Castleman et al (1974) has borne this out. These data suggest that there is a common source of sulfur compounds for the stratosphere of both the northern and southern hemispheres. Using elementary modeling calculations and the results of laboratory experiments, Castleman & Tang (1976/77), Davis et al (1979), and Moortgat & Junge (1977) have speculated that the stratospheric aerosol layer originates, at least in part, from SO_2 oxidation via OH. Other candidates for the origin of the sulfur component of the aerosol layer are COS (Crutzen 1976) and CS_2 as a precursor to COS [Sze & Ko 1979]. It is

still unclear to what degree the oxidation of the sulfur species is completely homogeneous (creating a supersaturation of H_2SO_4 with subsequent nucleation and condensation) or heterogeneous with the ultimate sulfate production occurring directly on preexisting particles.

Very little is known concerning the origin of the primary small particles that form as a result of processes following the generation of the precursors to the prenucleation embryos. It is almost certain that homogeneous nucleation does not operate in the atmosphere and that the more relevant processes are those termed heteromolecular and heterogeneous nucleation. Furthermore, in the stratosphere, processes that involve the interaction of more than one gaseous species participating in the formation of the condensed phase (particle) are certain to dominate under situations where new particle generation occurs.

The relative contribution of the various mechanisms proposed for the introduction of particles in the stratosphere has not been established. This problem is further complicated because the various nucleation processes and condensation compete for a limited supply of sulfur. Nevertheless, the general characteristics and extent of the stratospheric sulfate aerosol are reasonably well understood in terms of coagulation, condensation, evaporation, and sedimentation when a source for the generation of new particles is assumed.

ACKNOWLEDGMENTS

Literature Cited

Abraham, F. F. 1974. Monte Carlo simulation of physical clusters of water molecules. *J. Chem. Phys.* 61:1221-22

Arnold, F. 1980. Multi-ion complexes in the stratosphere—implications for trace gases and aerosol. *Nature* 284:610-11

Arnold, F., Fabian, R. 1980. First measurements of gas phase sulfuric acid in the stratosphere. *Nature* 283:55-57

Ausloos, P., Rebbert, R. E., Glasgow, L. 1977. Photo-decomposition adsorbed on silica surfaces. *J. Res. Natl. Bur. Stand.* 82:1-8

Baldwin, A. C., Golden, D. M. 1979. Heterogeneous atmospheric reactions: sulfuric acid aerosols as tropospheric sinks. *Science* 205:562-63

Bigg, E. K., Ono, A., Thompson, W. J. 1970. Aerosols at altitudes between 20 and 37 km. *Tellus* 22:550-63

Briant, C. L., Burton, J. J. 1975. Molecular dynamics study of the structure and thermodynamic properties of argon microclusters. *J. Chem. Phys.* 63:2045-58

Burgmeier, J. W., Blifford, I. H. 1975. A reinforced coagulation-sedimentation model for stratospheric aerosols. *Water, Air, and Soil Pollut.* 5:133-47

Cadle, R. D., Lazrus, A. L., Pollack, W. H., Shedlovsky, J. P. 1970. Chemical com-

position of aerosol particles in the tropical stratosphere. *Proc. Symp. Tropical Meteorol.* Section K-IV. 7 pp.

Cadle, R. D., Crutzen, P., Ehhalt, D. 1975. Heterogeneous chemical reactions in the stratosphere. *J. Geophys. Res.* 80:3381–85

Calo, J. M., Narcisi, R. S. 1980. van der Waals molecules possible roles in the atmosphere. *Geophys. Res. Lett.* 7:289–92

Carlon, H. R. 1979. Variations in emission spectra from warm water fogs: evidence for clusters in the vapor phase. *Infrared Phys.* 19:49–64

Castleman, A. W. Jr. 1974. Nucleation processes and aerosol chemistry. *Space Sci. Rev.* 15:547–89

Castleman, A. W. Jr. 1979. Nucleation and molecular clustering about ions. *Adv. Colloid Interface Sci.* 10:73–128

Castleman, A. W. Jr., Tang, I. N. 1972. Role of small clusters in nucleation about ions. *J. Chem. Phys.* 57:3629–38

Castleman, A. W. Jr., Tang, I. N. 1976/77. Kinetics of the association reaction of SO_2 with the hydroxyl radical. *J. Photochem.* 6:349–54

Castleman, A. W. Jr., Munkelwitz, H. M., Manowitz, B. 1974. Isotopic studies of the sulphate component of the stratospheric aerosol layer. *Tellus* 26:222–34

Castleman, A. W. Jr., Davis, R. E., Tang, I. N., Bell, J. A. 1975. Heterogeneous process and the chemistry of aerosol formation in the upper atmosphere. *Proc. Conf. Climate Impact Assess. Prog., 4th,* pp. 470–77

Castleman, A. W. Jr., Holland, P. M., Keesee, R. G. 1978. The properties of ion clusters and their relationship to heteromolecular nucleation. *J. Chem. Phys.* 68:1760–67

Chan, L. Y., Mohnen, V. A. 1980. The formation of ultrafine ion H_2O-H_2SO_4 aerosol particles through ion-induced nucleation process in the stratosphere. *J. Aerosol Sci.* 11:35–45

Cronin, J. F. 1971. Recent volcanism and the stratosphere. *Science* 172:847–49

Crutzen, P. 1976. The possible importance of CSO for the sulfate layer of the stratosphere. *Geophys. Res. Lett.* 3:73–76

Davis, D. D., Ravishankara, A. R., Fisher, S. 1979. SO_2 oxidation via the hydroxyl radical atmospheric fate of HSO_4 radicals. *Geophys. Res. Lett.* 6:113–16

Farlow, N. H., Hayes, D. M., Lem, H. Y. 1977. Stratospheric aerosols: undissolved granules and physical state. *J. Geophys. Res.* 82:4921–29

Farlow, N. H., Snetsinger, K. G., Hayes, D. M., Lem, H. Y., Tooper, B. M. 1978. *J. Geophys. Res.* 83:6207–11

Farlow, N. H., Ferry, G. V., Lem, H. Y., Hayes, D. M. 1979. Latitudinal variations of stratospheric aerosols. *J. Geophys. Res.* 84:733–43

Ferguson, E. E. 1978. Sodium hydroxide ions in the stratosphere. *Geophys. Res. Lett.* 5:1035–38

Friedlander, S. K. 1977. *Smoke, Dust, and Haze.* New York: Wiley. 317 pp.

Friend, J. P. 1966. Properties of the stratospheric aerosol. *Tellus* 18:465–73

Friend, J. P., Leifer, R., Trichon, M. P. 1973. On the formation of stratospheric aerosols. *J. Atmos. Sci.* 30:465–79

Friend, J. P., Barnes, R. A., Vasta, R. M. 1980. Nucleation by free radicals from the photooxidation of sulfur dioxide in air. *J. Phys. Chem.* 84:2423–36

Fuchs, N. A., Sutugin, A. G. 1971. Highly dispersed aerosols. In *Topics in Current Aerosol Research,* ed. G. M. Hidy, J. R. Brock, 2:1-60. New York: Pergamon

Gelbard, F., Seinfeld, J. 1979. The general dynamic equation for aerosols. *J. Colloid Interface Sci.* 68:363–82

Gmelins Handbuch. 1960. Schwefel teil. Berlin: Springer. 825 pp. (In German)

Gruner, P. 1942–61. In *Handbuch der Geophysik,* ed. F. Linke, F. Moller, Vol. 8. Berlin: Borntrager. 432 pp.

Gruner, P., Kleinert, H. 1927. In *Probleme der Kosmischen Physik,* Vol. 10. Hamburg: Henri Grand

Hale, B. N., Plummer, P. L. M. 1973. On nucleation phenomena I: a molecular model. *J. Atmos. Sci.* 31:1615–21

Hamill, P., Kiang, C. S., Cadle, R. D. 1977a. The nucleation of H_2SO_4-H_2O solution aerosol particles in the stratosphere. *J. Atmos. Sci.* 34:150–62

Hamill, P., Toon, O. B., Kiang, C. S. 1977b. Microphysical processes affecting stratospheric aerosol particles. *J. Atmos. Sci.* 34:1104–19

Heist, R. H., Reiss, H. 1974. Hydrates in supersaturated binary sulfuric acid-water vapor. *J. Chem. Phys.* 61:574–81

Hoare, H. R., Pal, P., Wegener, P. P. 1980. Argon clusters and homogeneous nucleation: comparison of experiment and theory. *J. Colloid Interface Sci.* 75:126–37

Hofmann, D. J., Rosen, J. M. 1977. Balloon observations of the time development of the stratospheric aerosol event of 1974–1975. *J. Geophys. Res.* 82:1435–40

Hofmann, D. J., Rosen, J. M. 1980. Stratospheric sulfuric acid layer: evidence for an anthropogenic component. *Science* 208:1368–70

Hogg, A. R. 1963. The Mount Agung eruption and atmospheric turbidity. *Aust. J. Science* 26:119–20

Hunten, D. M., Turco, R. P., Toon, O. B. 1980. Smoke and dust of meteoric origin in the mesosphere and stratosphere. *J. Atmos. Sci.* 37:1342–57

Inn, E. C. Y., Vedder, J. F. 1980. Measurements of stratospheric sulfur constituents. *Geophys. Res. Lett.* In press

Jaeger, H. L., Wilson, E. J., Hill, P. G. Russell, K. C. 1969. Nucleation of supersaturated vapors in nozzles. I. H_2O and NH_3. *J. Chem. Phys.* 51:5380–88

Junge, C. E. 1963. *Air Chemistry and Radioactivity.* New York: Academic. 382 pp.

Junge, C. E., Manson, J. E. 1961. Stratospheric aerosol studies. *J. Geophys. Res.* 66:2163–82

Junge, C. E., Chagnon, C. W., Manson, J. E. 1961. Stratospheric aerosols. *J. Meteorol.* 18:81–108

Keefe, D., Noland, P. J., Rich, T. A. 1959. Charge equilibrium in aerosols according to the Boltzmann law. *Proc. R. Irish Acad. A.* 60:27–45

Kiang, C. S., Hamill, P. 1974. H_2SO_4-HNO_3-H_2O ternary system in the stratosphere. *Nature* 250:401–2

Kiang, C. S., Cadle, R. D., Hamill, P., Mohnen, V. A., Yue, G. K. 1975a. Ternary nucleation applied to gas to particle conversion. *J. Aerosol Sci.* 6:465–74

Kiang, C. S., Cadle, R. D., Yue, G. K. 1975b. H_2SO_4-HNO_3-H_2O ternary aerosol formation mechanism in the stratosphere. *Geophys. Res. Lett.* 2:41–44

Lamb, H. H. 1970. Volcanic dust in the atmosphere, with a chronology and assessment of its meteorological significance. *Proc. R. Soc. London Ser. A.* 226:425–533

Lazrus, A. L., Gandrud, B. W. 1974. Stratospheric sulfate aerosol. *J. Geophys. Res.* 79:3424–31

Lazrus, A. L., Gandrud, B., Cadle, R. D. 1971. Chemical composition of air filtration samples of the stratospheric sulfate layer. *J. Geophys. Res.* 76:8083–88

Manson, J. E., Junge, C. E., Chagnon, C. W. 1961. *Chemical Reactions in the Lower and Upper Atmospheres.* New York:Interscience

Martin, L. R., Wrenn, A. G., Wun, M. 1978. *Chlorine Atom and ClO Wall Reactions Products.* Final report prepared for the National Science Foundation

McMurry, P. H., Friedlander, S. K. 1979. New particle formation in the presence of an aerosol. *Atmos. Environ.* 13:1635–51

Meinel, M. P., Meinel, A. B. 1963. Late twilight glow of the ash stratum from the eruption of Agung volcano. *Science* 142:582–3

Meyerott, R. E., Reagan, J. B., Jainer, R. G. 1980. The mobility and concentration of ions and the ionic conductibity in the lower stratosphere. *J. Geophys. Res.* 85:1273–78

Mirabel, P., Katz, J. L. 1974. Binary homogeneous nucleation as a mechanism for the formation of aerosols. *J. Chem. Phys.* 60:1138–44

Mohnen, V. A. 1971. Discussion of the formation of major positive and negative ions up to the 50 km level. In *Mesospheric Models and Related Experiments*, ed. G. Fiocco, pp. 210–19. Dordrecht. Holland: Reidel

Moortgat, G. K., Junge, C. E. 1977. The role of SO_2 oxidation for the background stratospheric sulfate layer in the light of new reaction rate data. *Pure Appl. Geophys.* 115:759–74

Mossop, S. C. 1964. Volcanic dust collected at an altitude of 20 km. *Nature* 203:824–27

Niki, H., Maker, P. D., Savage, C. M., Breitenbach, L. P. 1980. Fourier transform infrared study of the HO radical initiated oxidation of SO_2. *J. Phys. Chem.* 84:14–16

O'Brien, F. E. M. 1948. The control of humidity by saturated salt solutions. *J. Sci. Instrum.* 25:73–76

Olszyna, K., Cadle, R. D., de Pena, R. G. 1979. Stratospheric heterogeneous decomposition of ozone. *J. Geophys. Res.* 84:1771–75

Podzimek, J., Sedlacek, W. A., Haberl, J. B. 1977. Aitken nuclei measurements in the lower stratosphere. *Tellus* 29:116–27

Pruppacher, H. R., Klett, J. D. 1978. *Microphysics of Clouds and Precipitation.* Dordrecht, Holland: Reidel. 714 pp.

Reiter, E. R. 1971. *Atmospheric Transport Processes Pt2: Chemical Tracers.* AEC Critical Review Series, US Atomic Energy Commission. Division of Technical Information, Washington, DC

Rosen, J. M. 1971. The boiling point of stratospheric aerosol. *J. Appl. Meteorol.* 10:1044–46

Rosen, J. M., Hofmann, D. J., Singh, S. P. 1978. A steady-state stratospheric aerosol model. *J. Atmos. Sci.* 35:1304–13

Schuster, B. G. 1970. Detection of tropospheric and stratospheric aerosol layers by optical radar (LIDAR). *J. Geophys. Res.* 75:3123–32

Shedlovsky, J. P., Paisley, S. 1966. On the meteoritic component of stratospheric aerosols. *Tellus* 18:499–503

Skinner, L. M., Sambles, J. R. 1972. The Kelvin equation—a review. *J. Aerosol Sci.* 3:199–210

Stauffer, D., Kiang, C. S. 1977. Fisher's droplet model and nucleation theory. *Adv. Colloid Interface Sci.* 7:103–30

Sze, N. D., Ko, M. K. W. 1979. Is CS_2 a precusor for atmospheric COS? *Nature* 278:731–32

Toon, O. B., Pollack, J. B. 1973. Physical properties of stratospheric aerosols. *J. Geophys. Res.* 78:7051–59

Toon, O. B., Pollack, J. B. 1980. Atmospheric aerosols and climate. *Am. Sci.* 68:268–78

Toon, O. B., Turco, R. P., Hamill, P., Kiang, C. S., Whitten, R. C. 1979. A one-dimensional model describing aerosol formation and evolution in the stratosphere II. Sensitivity studies and comparison with observations. *J. Atmos. Sci.* 36:718–36

Turco, R. P., Hamill, P., Toon, O. B., Whitten, R. C., Kiang, C. S. 1979. A one-dimensional model describing aerosol formation and evolution in the stratosphere: I. Physical processes and mathematical analogy. *J. Atmos. Sci.* 36:699–717

Twomey, S. 1977. *Atmospheric Aerosols.* New York: Elsevier. 302 pp.

Viggiano, A. A., Perry, R. A., Albritton, D. L., Ferguson, E. E., Fehsenfeld, F. C.

1980. The role of H_2SO_4 in stratospheric negative-ion chemistry. *J. Geophys. Res.* In press

Volz, F. E. 1965. Note on the global variation of stratospheric turbidity since the eruption of Agung Volcano. *Tellus* 17:513–5

Volz, F. E. 1970. On dust in the tropical and mid-latitude stratosphere from recent twilight measurements. *J. Geophys. Res.* 75:1641–46

Volz, F. E., Goody, R. M. 1962. The intensity of the twilight and upper atmospheric dust. *J. Atmos. Sci.* 19:385–406

Yue, G. K. 1979. A quick method for estimating the equilibrium size and composition of aqueous sulfuric acid droplets. *J. Aerosol Sci.* 10:75–86

Zeisberg, F. C. 1928. Vapor pressures, boiling points and vapor compositions for the system H_2O-H_2SO_4-HNO_3. In *International Critical Tables*, ed. E. W. Washburn, 3:306–8. New York: McGraw-Hill

Zurek, W. H., Schieve, W. C. 1978. Molecular dynamics evidence for vapor-liquid nucleation. *Phys. Lett.* 67A:42–45

Zurek, W. H., Schieve, W. C. 1980. Multistep clustering and nucleation. *J. Phys. Chem.* 84:1479–82